PROGRESS REPORT

Period July 22, 1974 through September 21, 1974

# INVESTIGATION OF CRYSTAL GROWTH FROM SOLUTIONS

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
CONTRACT NUMBER NAS 8-28098

by

Professor Ichiro Miyagawa
Project Director
The University of Alabama



University, Alabama 35486 October 7, 1974

(NASA-CR-120510) INVESTIGATION OF CRYSTAL GROWTH FROM SOLUTIONS Progress Report, 22 Jul. - 21 Sep. 1974 (Alabama Univ., University.) 18 p
N74-76968
Unclas
00/99 53460

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# I. Progress During Reported Period

## A. Introduction

During the present reporting period most of the work done was concerned with preparation of a paper for publication on the results of the Rochelle salt growth experiment performed on Skylab-4. In addition, a ferroelectric hysteresis study was made on a chip from the Skylab crystal.

Although the analysis of the Skylab crystals is far from complete, we believe that publication of the results of the preliminary analysis is very important at this time. Comments and criticism from the scientific community are needed now, both for accurately interpreting the results of the present experiment and for making suggestions about possible future zero-gravity experiments. We hope that publication of these results will focus some attention on the need for more experiments done under these unique conditions.

## B. Preliminary Manuscript

A rough draft of our paper on the preliminary results of the Rochelle salt growth experiment performed on Skylab-4 has been reviewed by several scientists in the University community. The comments and suggestions of Dr. J. H. Bartlett, of the Physics Department and Dr. David Zatko of the Chemistry Department have been incorporated in the present version of the manuscript and are much appreciated. The version of the manuscript which follows is still being revised and improved so that eventually scientists who are not familiar with the general field of crystal growth can read and understand our paper.

Growth of Rochelle Salt Crystals on Skylab-4

Abstract. Rochelle salt crystals were grown on board Skylab-4 by Astronaut Col. Pogue. The microscopic and macroscopic characteristics of these crystals grown under zero-gravity conditions were compared to those of crystals grown in ground-based laboratories. Most of the defects found in the crystals were microscopic cavities which were quite regular in arrangement and orientation. Evidence which suggests the presence of a macroscopic long-range molecular force was also obtained from this experiment.

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Several workers (1) have suggested that the near zero-gravity environment available in recent manned orbital flights should be ideal for growing very high-quality crystals. Since gravity-driven convection currents in the growth solution are responsible for many types of defects found in earth-grown crystals, it was expected that a controlled temperature experiment could produce practically defect-free crystals in a near-zero gravity field. For this reason a growth experiment using Rochelle salt was performed for use on Skylab-4. Unfortunately, facilities for programmed temperature growth were not available for this experiment, and hence we could not control the temperature of the solution or the growth rate of the crystal. As a result, the crystals grown for us on Skylab-4 were not free of defects. Nevertheless, this experiment produced some interesting results which we present in this paper.

The ground-based preparation was made in the solution crystal growth laboratory of the Department of Physics, The University of Alabama. Large seed crystals of Rochelle salt (potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$, J. T. Baker, analytical reagent, 99.0% min. purity) were grown by slowly cooling a saturated aqueous solution, and granular Rochelle salt growth material was prepared by recrystalization from a saturated aqueous solution.

A 21.6 gram seed crystal and 8.4 grams of granular Rochelle salt were placed in an empty aluminum can similar to the ones used to heat and store food for the astronauts. This can was 3 cm deep and 10 cm in diameter, thus its volume was about 236 cc. The inside surface was coated with white teflon. The can was completely filled with a solution of Rochelle salt saturated at 25°C and sealed with a transparent plastic membrane top. The food can was further sealed with a "pull-top" aluminum lid at Swift and Company of Oak Brook, Illinois.

The growth experiment actually performed by Col. Pogue on the Skylab-4 mission is as follows: first the entire top of the pull-top can was removed from the food can, leaving the plastic membrane in place to confine the contents. The can was then heated to about 60°C for about 40 minutes in one of the units of the astronaut's food tray. Col. Pogue reported that all of the granular Rochelle salt and about 3/4 of the seed had dissolved when he removed the food can from the heater. Since no controlled-cooling device was available, Col. Pogue wrapped the can in some soft washcloths and towels in order to make the cooling rate as slow as possible. The wrapped can was then stored in a quiet place, and crystals were allowed to grow. Ground-based simulation experiments indicate that the solution in the can would have reached the cabin temperature of 25°C in about 6 hours. After two days, the can was unwrapped and the contents inspected through the membrane cover. Col. Pogue reported that there were many "nickel and dime" sized pieces of solid crystalline material located in the food can at that time. Unfortunately, because of the difficulty of observing these clear crystals against the white teflon coating of the food can, no photographs of this phase of the experiment were taken. It was decided to allow the crystals to grow for some additional time, so the can was rewrapped and stored in the same place. After 30 days of further growth, the can was unwrapped and the membrane cover was opened. Col. Pogue reported that the can now contained a single large crystal and some "slush". The crystal was recovered and the remaining material discarded. When the crystal was unpacked after completion of the mission it was discovered that it had broken into three large pieces and several small chips.

Table I lists weights and sizes of the recovered crystals. The combined weight of the crystalline material is about 12 grams, which is less than the weight expected from simulation experiments. One possible explanation for this small amount of recovered product is that because of the lack of convection currents the only transport process was diffusion, and the dissolved Rochelle salt molecules reached the surface of the growing crystal very slowly. Thus, even after 30 days of growth time, the solution was still supersaturated. Supporting evidence for this explanation is the "slush" the astronaut reported when he opened the food can to recover the crystal. Apparently, the solution was still supersaturated when the can was opened, and the shock of opening resulted in the production of these tiny crystals which appeared to the astronaut as a slush. It should be noted that in many ground-based crystal growth experiments, stirring the solution is necessary to insure that adequate material will reach the surface of the growing crystal. If stirring the solution is not practical, then gravity-driven convection currents may also suffice. In the present case, neither stirring nor convective forces were available to transport material to the growing crystals.

The crystal originally recovered in the cabin is believed to be one unit crystal. The photograph in Fig. 1 shows the three crystals #1-3 assembled into one large crystal. This conclusion is further confirmed by a photograph taken by Col. Pogue at the time the crystal was removed. Thus, most of the other small crystal chips, if not all of them, probably appeared when the large crystal was broken during re-entry or splash-down of the command module.

Figure 2 compares microscope photographs of crystal #2 with an earth-grown Rochelle salt crystal produced in our laboratory. Both crystals have defects that appear to be cavities when viewed with a low-power microscope. However, the cavities in crystal #2 appear to be far more regular than those in the earth-grown crystal. A typical cavity in crystal #2 was found to be a tube about 4 mm long and 0.1 mm in diameter. These tubular cavities shown in the upper photograph of Fig. 2 have their long axes in the direction of the c crystal axis. Almost all the defects in the crystals returned from Skylab-4 are tubes elongated in this way. There are a few spherical droplets of solution trapped in the long tubular cavities; but they are very small and occupy less than 1% of the cavity volume. It should be noted that we have occasionally grown Rochelle salt crystals which have a few tubular cavities in regions that are otherwise free of defects. However, no crystal grown in our laboratory has shown as many regularly arranged tubular cavities as those found in the Skylab crystal.

The crystal grown on board Skylab-4 is actually a collection of at least 5 component crystals (see Fig. 1). The figure shows that the c axes of the component crystals are parallel to each other. Further examination of the crystal reveals that the a and b axes of the component crystals are parallel or very nearly parallel to each other. In the case of an earth-grown crystal which consists of several components, the orientation of the axes of any component with respect to the axes of any other component is completely random.

The Skylab crystal is very fragile compared to those grown in ground-based laboratories. Small pieces or chips frequently break off when this crystal is held by forceps for examination. When it is possible to fit the broken chip back into the large crystal we find that the c axis of the chip is always parallel to that of the large crystal. We cannot determine if this is true for the a and b axes as well because of the small size of the chip. However, it is probable that all 3 axes of these chips are parallel to the corresponding axes of the large crystal. Thus, we believe that each of the 5 component crystals mentioned above is further a collection of many tiny crystals oriented with their corresponding crystal axes parallel to each other.

Rochelle salt is known to have an unusually large dielectric tensor component in the direction of its a crystal axis (2). This occurs in the temperature range around 25°C where most of the crystal growth is supposed to have occurred. Thus, it is conceivable that two Rochelle salt crystals would tend to orient themselves so that their a axes are parallel. No such orientation effect is expected for the b and c axes. Thus the large anisotropic dielectric tensor component would not satisfactorily explain the observed result.

Our observations on the Skylab crystal suggests the possibility of an attractive, long-range, orientation-dependent, molecular force between crystals. This force probably ranges over a few millimeters (the average separation of the "nickel and dime sized" crystalline pieces). The force also tends to orient the crystals such that corresponding axes are parallel when the crystals come close to each other in solution. Col. Pogue's report that the crystalline assembly appeared to have decreased in size during the 30 days in solution could be interpreted by utilizing this attractive force.

The large-looking assembly of crystal pieces originally formed probably was transformed into a smaller-looking crystal unit, through the process of mutual orientation and attraction of the component pieces. In a gravitational field, this long-range force effect would be prevented by convection currents.

Long-range molecular forces between macroscopic bodies, such as that surmised in the above discussion, have been studied by several investigators(3). The ranges of these forces observed in a ground-based laboratory is typically $10^{-4}$ to $10^{-3}$ mm. Several authors have attempted to formulate theories to explain these forces (4) although their efforts have been limited to the isotropic parts of these forces.

In conclusion, the results of our Skylab-4 crystal growth experiment provides the first experimental evidence of the forces on crystals grown from solution in a zero-gravity environment. We hope that subsequent experiments can control additional parameters such as temperature, growth rate, dissolved air in solution, pressure, and vibrations. Photographs of future growth experiments should also be valuable and answer many questions about the nature of the growth process.

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Table 1. Weights and sizes of the Rochelle salt crystalline material recovered from Skylab-4.

| CRYSTAL | WEIGHT | APPROXIMATE DIMENSIONS (cm) |
| --- | --- | --- |
| #1 | 8.73 grams | 4 x 3 x 0.5 |
| #2 | 2.82 grams | 2.5 x 1.5 x 0.5 |
| #3 | 0.50 grams | 1 x 1 x 0.5 |
| 16 chips | 0.2 grams total | 0.2 cm or less each |

## CAPTIONS FOR FIGURES

Fig. 1 Rochelle salt crystal grown on board Skylab-4. This photograph shows the three largest assembled into one unit.

Fig. 2. Microscope photographs of two Rochelle salt crystals. The upper photograph shows some of the microscopic defects in the Rochelle salt crystal grown on board Skylab-4 by Astronaut Col. Pogue. The lower photograph shows some defects in an earth-grown Rochelle salt crystal at about the same magnification for comparison.

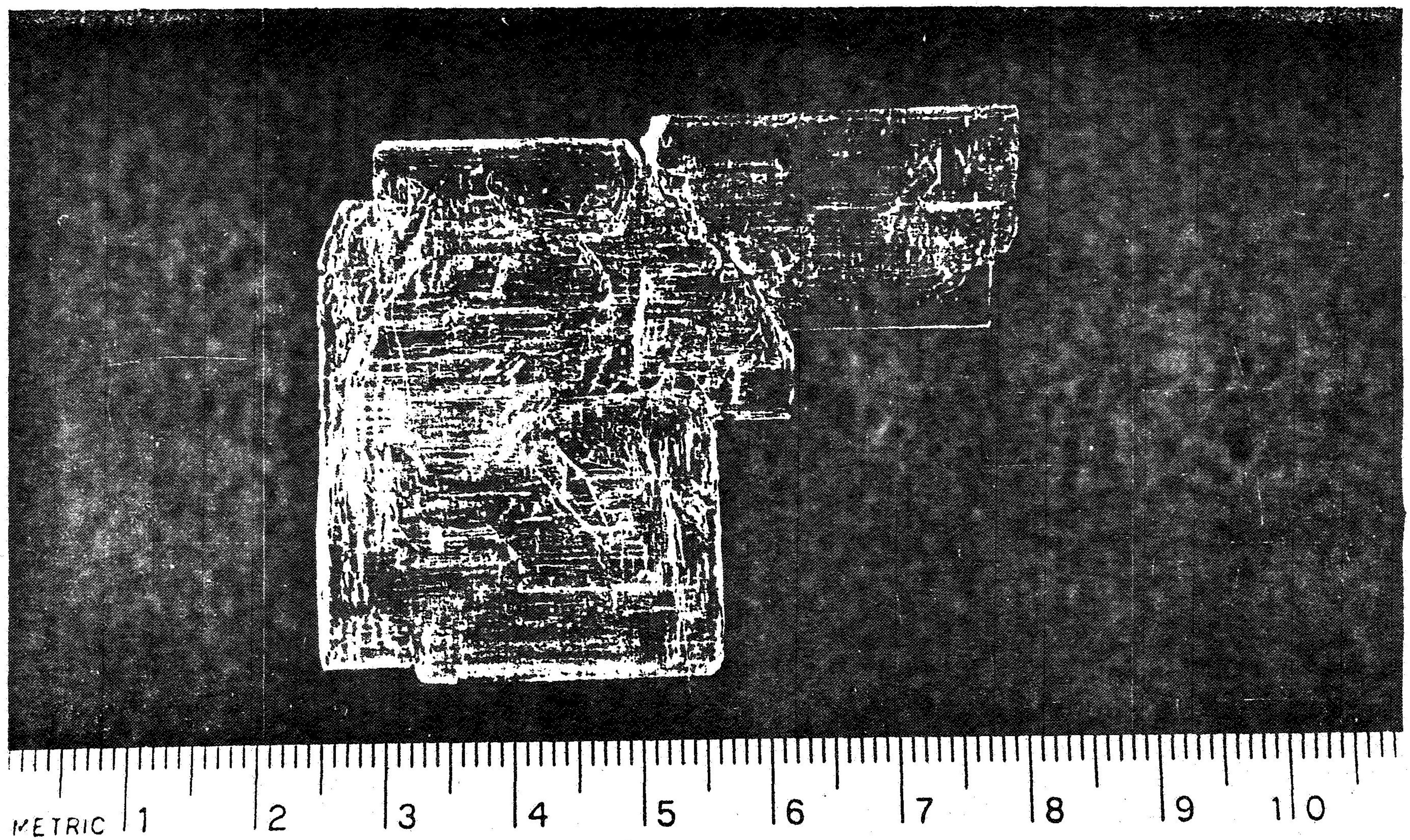



Figure 1

Figure 2

C. Skylab Crystal-Hysteresis

The apparatus used for measuring the S-value of the Skylab crystals is given in the previous bi-monthly progress report (6). A small chip from crystal #1 was used to measure the hysteresis of a part of the crystal. The chip was broken from the larger crystal sometime before it was returned to our lab. The orientation of its a axis, which must be determined in order to observe the hysteresis curve of the sample, was apparent from the way the chip fit back into the large crystal.

The hysteresis curve for the chip is shown in Fig. 3. The S-value calculated from this curve is 2.46. This number is larger than 1.36 which is the S-value reported for the bulk Skylab sample (6). Microscopic examination of the chip showed there were fewer cavities per unit volume than in the bulk sample. This is in agreement with our previous result that the S-value of a sample containing many cavities would appear to be low, even if the quality of the sample is excellent (6).

II. Work Planned

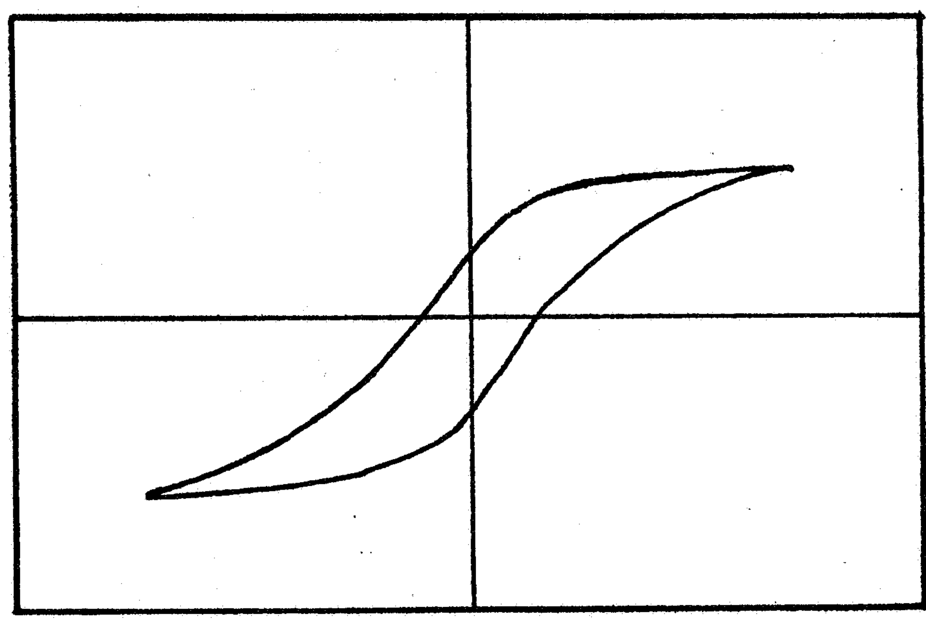
Work will continue on the construction of a machine to cut and slice a sample from the Skylab crystal for the purpose of measuring its hysteresis curve. A machine for drilling and cutting fragile crystals has been built and is being tested. It has successfully drilled very small holes in small, fragile crystals of L-alanine and TGS.

Theoretical analysis on the results of the hysteresis measurements on the Skylab crystal will continue.

III. Expenditures

Man-hours expended through September 22, 1974 - 10 months

Cost expenditures - $9,369.



## IV. Distribution

Copies of this report were mailed to National Aeronautics and Space Administration, George C. Marshall Space Flight Center, Marshall Space Flight, Alabama 35812 to the codes and in the quantities listed below. A copy of the transmitted letter showing distribution of the reports shall be furnished to AP13.

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| AT01 | 1 | 1 |
| ES12 | 12 | 32 + Repro |
| EM34 | 1 | 1 |
| APPLICABLE ONRRR | 1 | 1 |

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1. L. W. Spradley and Chien Fan, A Study of Natural Convection in Low Gravity Solution Growth of Rochelle Salt Crystals (LMSC-HREC D225365, Lockheed Missiles and Space Company, Huntsville, Alabama October, 1971); Ting L. Chu, Physical Phenomena Related to Crystal Growth in the Space Environment (NAS1-11869, Electronics Sciences Center, Southern Methodist University, Dallas, Texas, November, 1972); I. Miyagawa, Investigation of Crystal Growth from Solutions (NAS 8-28098, The University of Alabama, University, Alabama, February, 1973).

2. See for example: F. Jona and G. Shirane, Ferroelectric Crystals (The McMillan Company, New York, 1962), p. 282.

3. B. V. Deriagin and I. I. Abrikosava, Soviet Phys. JETP 3, 819 (1955); ibid. 4, 2 (1957); A. I. Bailey and H. Daniels, J. Phys. Chem. 77, 501 (1973).

4. H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948); E. M. Lifshitz, Soviet Phys. JETP 2, 73 (1956); E. A. Power, Advan. Chem. Phys. 12, 167 (1967).

5. We thank Dr. Ikuo Suzuki for his assistance in the preparation of seed crystals and solutions for this experiment. This work was supported by the NASA contract, NAS 8-28098.

6. Progress Report, Period May 22, 1974 through July 21, 1974, Investigation of Crystal Growth From Solutions, NASA contract number NAS 8-28098.